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HEAT TOLERANCE OF GREEN GLASS CONTAINERS

A. B. Atkarskaya,^{1,3} D. A. Raspopov,² P. V. Chartii,¹ and V. G. Shemanin¹

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The effect of individual production factors on the heat tolerance of glass containers is studied. It is shown that the use of quartz raw material distinguished by its fineness from the material adopted for a technological process in a given glass-making furnace can result in massive production rejects, consisting in the appearance of seeds and heat intolerance. The phenomenon is explained from the standpoint of oscillations of the heat tolerance index of molten glass.

Key words: glass containers, heat tolerance, heat tolerance index, quartz raw material.

Glass containers have undoubted advantages over plastic containers. This is because glass possesses high chemical stability with respect to different corrosive media. For this reason the food industry prefers glass containers.

Before use glass containers pass through a mandatory preparation process, including washing and drying. The criterion for success of this operation is heat resistance, determined by the temperature difference (from 35 to 50°C depending on the area of application) that an article must withstand without breaking.

The objective of the present work is to study the effect of certain technological factors on the heat tolerance of glass containers.

The object chosen for investigation is a green bottle produced in a multi-ton glass-making furnace under the conditions of continuous commercial production.

The green color of the glass container is due to chromium compounds which are specially introduced into the mix in the amounts 0.2%⁴ in terms of Cr₂O₃. At the same time, together with the natural raw materials, which are contaminated with various impurities, considerable amounts of Fe₂O₃ (about 0.2%) are present in the molten glass. Chromium and lead are *d* elements with variable valence and in glass each one can be present in degrees of oxidation: 6+, 3+ and 3+, 2+, respectively, for Cr and Fe (Fig. 1) [1]. Hexavalent chromium and trivalent iron exhibit absorption bands in the short-wavelength part of the spectrum and impart a yellow color to the glass. Trivalent chromium with absorption

maxima in the visible range at 460 and 640 nm color glass in bright, saturated green and bivalent iron with a diffuse band near 1000 – 1100 nm imparts a dingy bluish-green color.

The actual color of green container glass is due to the combined effect of two pigments — chromium and iron.

When present together in the melt chromium and iron affect one another according to Weil's oxidation-reduction se-

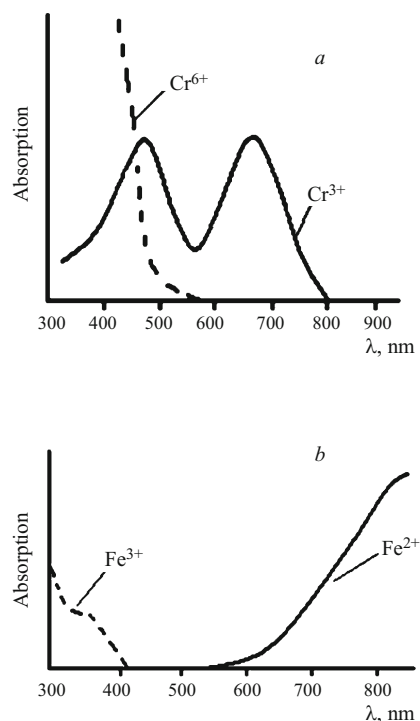


Fig. 1. Absorption spectra of silicate glasses, colored with (a) chromium and (b) iron.

¹ Novorossiisk Polytechnic Institute, Affiliate of Kuban State Technological University, Novorossiisk, Russia.

² "Sputnik" JSC, Krasnodar, Russia.

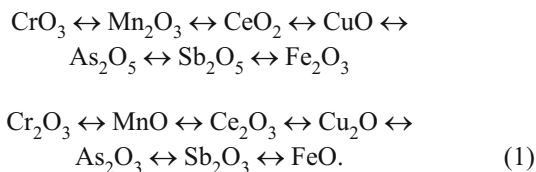
³ E-mail: atkarsk06@mail.ru.

⁴ Here and below — content by weight.

TABLE 1. Effect of the Technology Parameters on the Equilibrium of the Oxide Forms of Iron in Glass

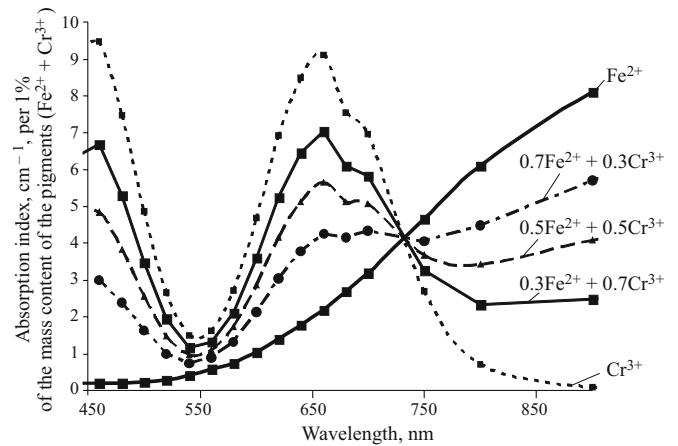
Parameter	Shift of the equilibrium $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$
Oxide composition of the glass	Left-ward — as the molar concentration of the acidic ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) and decrease of the basic ($\text{RO} + \text{R}_2\text{O}$) oxides, i.e. as $K_{\text{base}} = \frac{\text{R}_2\text{O} + \text{RO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$ decreases [8]
Iron concentration in glass	Left-ward — as the total iron concentration decreases
Oxidation-reduction and temperature-time regime of glassmaking and extraction	Left-ward — with increasing temperature and duration of the glass-making process; right-ward — with increasing oxygen partial pressure in the furnace atmosphere
Presence of other variable-valence elements	In accordance with Weil's oxidation-reduction series (1)
Oxidation-reduction potential of raw materials, cullet, mix, form of the raw materials	Depending on the concentration of the oxidizing and reducing (for example, organic) impurities and contaminations. Left-ward — with increasing concentration of carbonates in the mix
Mix/cullet ratio	Right-ward — with increasing cullet fraction

ries [1]: every oxide appearing on the left-hand side in a higher valence form oxidizes any oxide standing on the right-hand side and in a state of lower valence:



Therefore the equilibria $\text{Cr}^{6+} \leftrightarrow \text{Cr}^{3+}$ and $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ are intercoupled. For this reason, there is every reason to expect that an increase of the mass content of bivalent iron and its role, calculated as the ratio of the concentration of the bivalent iron to its total content, will be symbatic to the increase of the fraction and content of the hexavalent chromium in glass. The consequence will be a change of the spectral curve of the glass, as shown in Fig. 2. These plots were obtained by a computational method from known values of the absorption indications with total content 1% of bivalent iron and trivalent chromium in alkali-alkali-earth-silicate glass. They show that a systematic increase of the content of bivalent iron will decrease the intensity and smoothing of the absorption bands in the visible range (450–720 nm), while the loss of light in the near-IR part of the spectrum (720 and farther nm) will increase considerably.

Aside from the transformation of the spectral curves as the Fe^{2+} concentration increases, the index of the diather-

**Fig. 2.** Spectral curves of the absorption indices of iron and chromium when present simultaneously in alkali-alkali-earth-silicate glass.

mancy (ID) of the melt, calculated according to the expression [2, 3]

$$\text{ID} = 10^{-1} \tau_{1100}, \quad (2)$$

where τ_{1100} is the light transmission of a 0.01 m thick glass sample at wavelength 1100 nm, in %, will become worse.

At furnace temperatures from 1500 to 1600°C the maximum radiation of the flame and dome lies near 1500 nm [4]. The presence of bivalent iron in the melt affects the radiant thermal conductivity and the thermal diffusivity along the depth of the tank. The higher the Fe^{2+} content and the lower the diathermancy index, the worse the IR radiation penetrates into the molten glass during glassmaking and heat is removed from its inner layers during cooling.

Therefore the growth of the FeO concentration caused by an increase of the content of iron oxides or by an uncontrollable leftward shift of the equilibrium $\text{Fe(II)} \leftrightarrow \text{Fe(III)}$ can complicate the glassmaking and extraction processes and lead to the appearance of flaws and chemical and thermal nonuniformity of the glass. Aside from the spectral and associated color characteristics, according to the data of [5] the service properties of glass, such as the strength and chemical and thermal stability, are degraded. The action of Fe^{2+} on the absorption in the IR region of the spectrum likewise has a direct effect on the rate and uniformity of the solidification of glass articles as the articles are formed [6, 7].

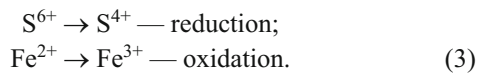
Thus, efficient execution of the technological process and regulation of the characteristics of any kind of glass are unthinkable without stabilization of the FeO content, which depends on the position of the equilibrium $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ and the total iron concentration in the glass. The equilibrium $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ forms under the simultaneous action of a number of parameters of the technology [5] (Table 1).

In green container glass fined with sodium sulfate the equilibrium of the oxide forms of iron is affected not only by

TABLE 2. Technical Conditions for Sand

Index	For raw materials of grades			
	B-100-1	B-100-2	PB-150-1	PB-150-2
Silicon dioxide (SiO_2) mass fraction, %, not less than	98.5	95.0	98.0	95.0
Iron oxide (Fe_2O_3) mass fraction, %, not greater than	0.10	0.10	0.15	0.15
Aluminum oxide (Al_2O_3) mass fraction, %, not greater than	0.6	2.0	1.5	2.0
Moisture mass fraction, %, not greater than:				
in enriched sands	0.5	0.5	0.5	—
in non-enriched sands	7.0	7.0	7.0	7.0
Heavy mass fraction ($d > 2.9$) in enriched sands, %, not greater than	Not standardized			

Cr_2O_3 introduced into the mix as a pigment but also by sulfur. The following oxidation-reduction interaction between iron and sulfur can occur in the melt [9]



Sulfur with degree of oxidation 4+ forms with oxygen, which is always present in the furnace atmosphere, SO_2 , which is insoluble and therefore easily evaporates from the molten glass [4]. For this reason, if the concentration of the fining agents is stable, the residual SO_3 in the glass makes it possible to evaluate approximately the effectiveness the oxidation of iron in the melt: the more SO_3 , the higher the FeO concentration.

Under market conditions and especially during the economic crisis, every producer looks for ways to decrease productions costs. This is most easily achieved by lowering the cost of raw materials, for example, by lowering its grade. Since container glass is 70% SiO_2 , the greatest effect can be achieved by replacing sand, for example, grade B-100, by a cheaper grade PB-150. The GOST 22551 quality parameters are presented in Table 2.

It follows from Table 2 that for 70% content of SiO_2 the use of PB-150 sand instead of B-100 sand can additionally enrich the glass by approximately $0.7 \times (0.15 - 0.10)\% = 0.04\% \text{Fe}_2\text{O}_3$.

According to GOST 22551 the oxidizing and reducing impurities in quartz raw materials for glassmaking are not standardized, and they also contribute to the formation of the equilibrium of the oxide forms of iron. Specifically, organic impurities have a reducing effect, and their concentration can be judged from the calcination losses (CL). In the present case (Table 3) they are 2–4 times larger in PB-150 sand than in B-100 sand.

Therefore such a change in the raw material results in high concentration in iron oxide and organic (reducing) impurities in the mix. Combined, these two factors favor a higher FeO mass fraction and lower diathermancy of the molten glass.

Periodic loading into a continuously operating commercial furnace of a mix prepared with different grades of sand (or an arbitrary mixture of them) can give rise to discernible fluctuations of the content of total iron, bivalent iron, and diathermancy; this can complicate the technological process of making glass and extracting molten glass and can cause product rejection.

Figure 3 demonstrates real consequences of loading into a multi-ton glassmaking furnace producing green container glass portions of mix prepared using B-100 and PB-150 sands and their mixtures, and it shows the change according to a chemical analysis of the concentrations of total iron (in terms of oxide) and sulfur (in terms of SO_3). The solid vertical lines show the moments at which rejects appear (non-heat-tolerant containers).

Over the time period considered the Fe_2O_3 content in glass showed a trend toward a negligible decrease (see trend line, Fig. 3), changing on separate days from 0.18 to 0.28%, which is a consequence of using different brands of sand — B-100 and PB-150.

Even though the concentration of fining agents in the mix remained constant, the SO_3 content fluctuation from 0.09 to 0.24%, showing a tendency toward increasing negligibly (see the Fig. 3). This could be due to a shift of the oxidation-reduction equilibrium between iron and sulfur toward hexavalent sulfur and bivalent iron (3), respectively. Therefore, with high probability the Fe^{2+} concentration showed an inadmissible tendency to increase and, correspondingly, the diathermancy of the glass to decrease.

TABLE 3. Sand Properties

Parameter	Sand grade		
	B-100-1	PB-150-1	
		1st batch	2nd batch
Calcination losses, %	0.13	0.26	0.49
Visual characteristic	Color light-yellow	Color gray-tinged saturated yellow	

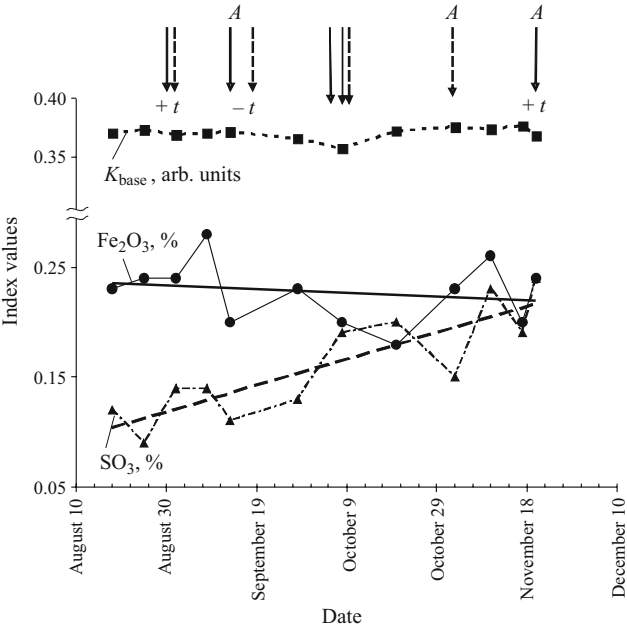


Fig. 3. Change in time of the content (%) of Fe₂O₃, SO₃ in glass. The solid arrows show the times when rejects appear according to heat-tolerance and the discontinuous lines show the rejects according to the quality of the product. + *t*) correction made in the furnace temperature, – *t*) same in the direction of lowering the temperature; *A*) the spectral characteristics of the glass are analyzed.

To confirm this supposition some properties of individual good samples and samples rejected on the basis of diathermancy of the glass were compared (Table 4).

It follows from Table 4 that the rejected glass is harder, since it is characterized by lower values of *K*_{base}, calculated from the expression presented in Table 1. During these periods the furnace temperature was increased in a regular manner from 1510 – 1515 to 1520 – 1535°C. Taken together (see Table 1) the decrease of *K*_{base} and increase of temperature had a large effect on the right-ward shift of the equilibrium

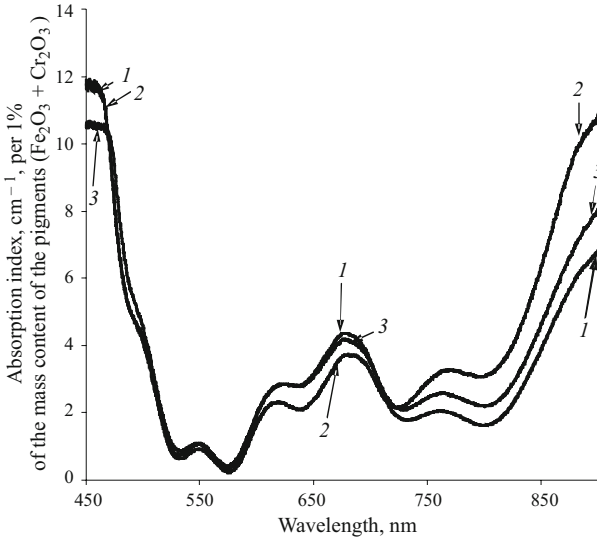


Fig. 4. Spectral curves of the absorption index of high-quality and diathermancy rejected green container glass: 1) high-quality glass; 2) rejected glass.

Fe³⁺ ↔ Fe²⁺ and the associated decrease of the diathermancy of the melt.

The temperature fluctuations in the furnace are also fraught with heating of the deep layers, deplete of oxygen and enriched with bivalent iron [5]. These layers possess a high reducing potential and low diathermancy, so that adding them to the molten glass of the working flow can give rise to secondary foaming, the appearance of seeds in the glass, and degradation of the distribution of the molten glass in articles, for example, in the form of single-sided fillings, which was found during the appearance of unacceptable product. At the extraction stage the nonuniformity of the glass mass with respect to diathermancy was expressed by the appearance of a dark band in a drop.

The spectral curves (Fig. 4) attest to the dependence of the heat-tolerance on the irregular right-ward displacement

TABLE 4. Some Parameters of the Technological Process and Glass Quality

Process and glass parameters	Product characteristics		
	high-quality	rejected	rejected
<i>K</i> _{base}	0.378	0.373	0.369
Maximum glass-making temperature, °C	1510 – 1515	1535	1520 – 1525
Mass fraction, %:			
Fe ₂ O ₃	0.23	0.20	0.24
SO ₃	0.15	0.11	0.24
Absorption index, cm ^{–1} per 1% (Fe ₂ O ₃ + Cr ₂ O ₃) mass fraction, at wavelengths:			
680 nm	4.3	4.2	3.7
900 nm	6.8	8.1	10.9
Color	Green	Green with yellow tinge	Green with yellow tinge

of the intercoupled equilibria $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ and $\text{Cr}^{3+} \leftrightarrow \text{Cr}^{6+}$ and an increase of the concentration of FeO in glass: in high-quality glass the intensity of the Cr^{3+} absorption band at 660 – 670 nm is higher and that of Fe^{2+} at 800 – 900 nm is lower than in glass rejected due to diathermancy (see Table 3).

Figure 2 also confirms the shift in the equilibria of iron and chromium oxides.

Comparing the results of Table 3 and Fig. 3 shows that the total iron concentration in high-quality glass is higher, but the SO_3 content is lower than the average values, so that the growth of FeO as a result of an increase of the iron content is probably compensated by the left-ward shift of the equilibrium $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$.

Diathermancy rejected glass is characterized by higher concentrations of total iron and SO_3 , differing substantially from the average values. For this reason, in such glass the FeO content is elevated and the diathermancy is depressed.

Therefore, thermal resistance decreases because of the concentration fluctuations of bivalent iron in glass, caused by loading into a tank glassmaking commercial furnace a mix prepared using sand with different degrees of purity with respect to iron and consumable impurities.

The following conclusions can be drawn in this basis:

- periodic use is inadmissible in the technology for producing green glass containers using quartz raw materials (sand) with elevated, relative to the levels adopted in a given glassmaking system, content of iron oxide and consumable impurities;
- use in a commercial glassmaking furnace of quartz raw material of different grades in the glassmaking process could be the reason for secondary foaming of the molten glass, degradation of the glass distribution during the formation, and appearance of non-heat-tolerant production;
- when high- or low-quality quartz raw materials, as compared with that adopted for the given technological pro-

cess, are periodically introduced the FeO concentration in the molten glass must be stabilized by adjusting the content of sodium sulfate in the mix.

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